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(54) Anodizing metals

(57) Valve metals eg Al, Ti, Ta, Zr, Nb and valve metal based alloys are anodized efficiently in a substantially non-aqueous formation electrolyte comprising a polar aprotic solvent and an electrolyte-soluble source of phosphate ions to provide high quality dielectric oxide coatings.

Titanium and titanium based alloys may be anodised at a current density of not greater than 2 milliamperes/cm^2. Preferred formation electrolytes for use in this process contain phosphoric acid and an acid-ionizing amine eg pyridine or urea or tetramethyl urea and have resistivities in the range of 1,000-30,000 ohms per cubic centimeter and breakdown voltages in excess of 200 volts.

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SPECIFICATION

Method of anodizing metals

This invention relates to an electrochemical process for anodizing metals. More particularly, this invention relates to a process for forming a dielectric oxide film or coating on valve metals. It has particular application to titanium and titanium based alloys.

For several decades now anodized (metal oxide coated) valve metals have been used as electrodes in commercially produced electrolytic capacitors. Since the electrode metal oxide coating functions essentially as an insulator, the electrical characteristics of anodized metal electrode capacitors are determined to a large extent by the thickness, quality, stability and inherent dielectric properties of the metal oxide layer. Both the patent and non-patent literature reflect a significant ongoing research and development effort directed to the definition of improved methods for anodizing valve metals and valve metal alloys. Of course, the ultimate goal of these efforts is the production of less expensive, more efficient and more dependable electrolytic capacitors. It is recognised, however, that antecedent to the achievement of that goal is the need to develop efficient anodization process techniques which can be applied to a wide range of valve metal and valve metal alloys to provide suitable capacitor electrodes having a thin, continuous, dielectric metal oxide coating which is chemically and thermally stable and adherent to the metal surface.

The anodization of valve metals, i.e. the formation of a dielectric oxide layer at the surface of said metals, is accomplished by the chemical or, preferably, the electrochemical oxidization of metal atoms at and adjacent to the metal surface. Numerous electrochemical processes for anodizing valve metals have been developed. Electrochemical anodization processes are typically carried out in an electrolytic cell by immersing the valve metal in an electrolyte (the formation electrolyte) and connecting it electrically to the positive pole (anode) of an electric current source. As electric current is passed through the electrolytic cell, surface metal atoms of the valve metal anode are oxidized to form a metal oxide coating on the metal surface. Routinely the voltage across the electrolytic cell is gradually increased to maintain current flow as the insulating metal oxide layer is built up on the anode.

Such art-recognised electrochemical anodization processes are characterised by the use of aprotic, usually aqueous, formation electrolytes containing one or more oxide-forming ionogens. The majority of such art-recognised electrochemical processes for anodizing valve metals are further characterised by relatively low efficiency and limited application with respect to the scope of valve metals effectively anodized by said processes. For example, solutions of phosphoric acid and/or phosphates (e.g., ammonium phosphates) in water or water-ethylene glycol mixtures have been used for decades to anodize tantalum and aluminium metals. When such solution are used as formation electrolytes to anodize titanium, a highly hydrated and very electrically leaky oxide film results. The electrical leakiness of such titanium oxide films formed in aqueous or aqueous ethylene glycol solutions is evidenced by the formation of large quantities of gas at the oxide/formation electrolyte interface. Gas evolution during anodization results in low process efficiency.

Accordingly it is an object of the present invention to provide an efficient anodization process having application to a wide variety of valve metals and valve metal based alloys.

Another object is to provide an electrochemical method for forming thin, continuous, metal-adherent, dielectric oxide films or coatings on valve metals and valve metal based alloys.

Another object of this invention is to provide an efficient electrochemical anodization process which employs a substantially non-aqueous, polar, aprotic, formation electrolyte.

A further object of the present invention is to provide an improved electrochemical anodization process for titanium and titanium based alloys which efficiently provides high quality dielectric oxide films.

Another object of the present invention is to provide for use in capacitors an improved anodized valve metal electrodes, which consistently exhibit high unit capacitance per unit area.

One further object of the present invention is to provide improved anodized valve metal electrode capacitors.

The present invention in its broadest aspects contemplates a method for anodizing valve metals using a substantially non-aqueous, polar, aprotic formation electrolyte containing an ionogen comprising phosphoric acid or an electrolyte-soluble phosphoric acid salt. In a preferred embodiment the substantially non-aqueous formation solvent contains phosphoric acid and, in addition, urea or a water soluble substituted urea, or up to three equivalents of an electrochemically stable amine base for each equivalent of phosphoric acid in the formation electrolyte.

The preferred present anodizing method provides an efficient means for forming high quality, uniform, metal-adherent oxide films on valve metals. Capacitors assembled from titanium and titanium based alloy electrodes anodized in accordance with the present invention exhibit a significant capacitance advantage when compared to capacit rs assembled using titanium electrodes anodized in accordance with prior art (aqueous formation electrolyte) anodizati n processes.

The present invention in another aspect is directed to a process for electrochemically forming a dielectric oxide film on a valve metal comprising subjecting said valve metal t electrolytic anodic oxide f rmation conditions in a substantially non-aqueous formation electrolyte comprising a polar apr tic solvent

and an ionogen comprising phosphoric acid or an electrolyte-soluble phosphate salt, said electrolyte having a resistivity between 1,000 ohms and 30,000 ohms per cubic centimeter at 25°C.

The present process can be used to anodize valve metals or valve metal based alloys to provide a thin, uniform, impervious, metal-adherent oxide film on the metal surface. Exemplary of valve metals to which the present process can be applied are aluminium, titanium, tantalum, zirconium, niobium, and alloys based on one or more of those metals with other polyvalent metals, including known amorphous alloys available through rapidly cooled metals technology. The metals may be in any desired form, for example, a flexible or rigid sheet or strip, foil, wire or a porous-sintered slug. As will be recognised by those skilled in the art, metal foils and metal sheets anodized in accordance with the present process are particularly useful for the construction of capacitors in accordance with known capacitor construction techniques.

The present anodization process finds particular application for anodic oxide formation on titanium and titanium based alloys. Titanium, as a material for capacitor electrodes, offers several significant advantages over the more commonly used valve metals aluminium and tantalum. Titanium is cheaper and much lighter than tantalum (density of 4.5 vs. 16.6 gm/cc) and therefore can potentially give much greater capacitance per given weight or cost of metal. Moreover, titanium is known to form a tough, corrosion resistant oxide of high dielectric strength. In spite of the potential advantages offered by anodized titanium electrodes, the limitations of existing anodizing process technology has precluded extensive commercial use of titanium electrodes in capacitors. When titanium metal is anodized using art-favoured aqueous or aqueous ethylene glycol formation electrolytes containing phosphoric acid, a highly hydrated and very electrically leaky oxide film results. The "electrical leakiness" of such titanium oxide films results in low current efficiencies due to the formation of large quantities of gas at the metal oxide/formation electrolyte interface.

The inefficiency of prior art anodization processes carried out in aqueous formation electrolytes and the formation of hydrated leaky oxide film on titanium and titanium alloys is avoided by the process of the present invention which employs a substantially non-aqueous formation electrolyte. The formation electrolyte utilized in the present process comprises a polar aprotic solvent and an ionogen comprising phospheric acid or an electrolyte-soluble phosphate salt. For the purposes of this invention the degree of "aprotic" behaviour of a polar solvent may be determined by the addition of a small amount (suitably 1 or 2 grams) of granular ammonium carbonate to a 1%-5% concentrated phosphoric acid solution in the polar solvent to be tested. A solvent containing this percentage of concentrated phosphoric acid and displaying little or no reaction with ammonium carbonate is sufficiently aprotic for the purposes of this invention. Carbon dioxide will be generated in visible quantities in those solvents which are not suitable as the polar aprotic solvent component of formation electrolytes used in the present process. Exemplary of polar aprotic solvents found suitable for use in the present process for dimethylformamide, dimethylsulfoxide, N-methyl-2-pyrrolidone, and 4-butyrolactone. For practical purposes the polar aprotic solvent should have a relatively high boiling point and a low room temperature viscosity.

The term "substantially non-aqueous" used to define the formation electrolyte used in the present process means that the electrolyte should contain less than about 2% water. While the presence of some water in the formation electrolyte is important for the electrolyte oxide formation process, the amounts of water typically present in commercially available solvents used as the polar aprotic solvent component and in the phosphoric acid component of the formation electrolyte suffice to provide whatever minimum amounts of water are required for oxide formation.

Phosphoric acid or, more specifically, the phosphate ion has been found to be the best ionogen for use in the present process. Sufficient phosphoric acid or formation electrolyte soluble phosphate salt is added to the formation electrolyte in an amount sufficient to lower the resistivity of the electrolyte between 1,000 ohms and about 30,000 ohms per cubic centimeter at 25°C.

The factors governing the selection of an appropriate phosphate salt ionogen for the formation electrolyte include only the stability of the salt cation during the oxide formation process and solubility of the phosphate salt in the formation electrolyte and in water. Of course, the phosphate salt must have sufficient solubility in the formation electrolyte to allow salt concentrations sufficient to lower electrolyte resistivity to within the range specified above for the present process. The phosphate salt should also be sufficiently water soluble to allow salt residues to be water-washed from the surface of the anodized metal following the anodizing process. Without some degree of water solubility it is difficult, if not impossible to remove salt residue from etch tunnel of foil or from the internal portions of anodized sintered-metal slugs.

Suitable phosphate salts are the monohydrogen and dihydrogen phosphate salts formed by the reaction of phosphoric acid and weak amine bases including pyridine, quinoline, aniline, toluidine, semicarbazide and substituted derivatives thereof. The nature of substituents on such bases is not critical provided that the phosphate salts of said bases are soluble and substantially stable in th formation electrolyte, and provided further that they have some degree f water solubility. Of those ph sphate salts useful in the present process, pyridinium phosphate is preferred. The phosphate salts can be prepared using art-recognised techniques and thereafter dissolved in the formation electrolyte, or they can b formed *in situ* by th reaction of phosphoric acid and an amine base in the electrolyte in accordance with the preferred embodiment of the present invention discussed hereinbelow.

Phosphoric acid is itself a preferred formation electrolyte ionogen for the present process. It can be

employed alone or in combination with one or more of the below-described amine compounds which promote phosphoric acid dissociation to lower electrolyte resistivity and which buffer the acidity of the substantially non-aqueous polar aprotic formation electrolyte. Because of the substantially non-aqueous aprotic nature of the electrolyte, phosphoric acid does not ionize to the same extent to which it ionizes in aqueous aprotic electrolytes commonly used for oxide formation. The resistivity of the formation electrolyte is proportional to the degree of ionogen ionization. Therefore, higher concentrations of phosphoric acid are required in the present substantially non-aqueous polar aprotic formation electrolytes to lower the electrolyte resistivity to the levels necessary for practical current densities during the formation process. When phosphoric acid is used alone as the ionogen in a formation electrolyte for the present process, sufficient phosphoric acid is added to bring the electrolyte resistivity into a range of about 10,000 ohms to 30,000 ohms.

While an electrolyte resistivity below 10,000 ohms/cm³ can be achieved through the addition of increased amounts of phosphoric acid the advantage of lower solution resistivities (i.e., higher available anodization current densities) must be balanced against the effect which the added amounts of phosphoric acid has on the breakdown voltage of the electrolyte or, more particularly, the electrolyte reactivity with the metal during formation. The breakdown voltage of the formation electrolyte is the voltage at which gassing and/or scintillation (sparking) is observable at the anode. Generally speaking, as the phosphoric acid concentration is increased, both the resistivity and the breakdown voltage for the formation electrolyte is decreased.

Ideally the formation electrolyte should have breakdown voltage higher than the anodization (forming) voltage required to achieve acceptable dielectric coatings. For the present process it is preferred that the formation electrolyte exhibit a breakdown voltage greater than about 200 volts.

In a preferred embodiment of the present invention the formation electrolyte contains phosphoric acid and, in addition, urea, a water soluble substituted urea, or up to three moles of an organic amine base per mole of phosphoric acid in the formation electrolyte. The amine bases are selected from amine bases which are stable under the electrochemical anodization conditions of this process and which form phosphate salts soluble in both the formation electrolyte and water. The amine additives are used effectively to lower the resistivity of the present formation electrolytes containing given amounts of phosphoric acid. Thus phosphoric acid concentration in the formation electrolyte can be minimised, i.e. held within a concentration range associated with a preferred high electrolyte breakdown voltage, while at the same solution resistivity can be lowered to allow for higher current densities during the anodization process. Moreover, the added organic amine effectively reduces electrolyte "acidity" and thereby serves to minimise etching of the metal surface during anodization.

Examplary of organic amine bases which can be employed in the present formation electrolytes to reduce electrolyte resistivity and acidity are pyridine, quinoline, aniline, toluidine, semicarbazide and substituted derivatives thereof which form phosphate salts soluble in both the formation electrolyte and water.

When an amine is employed with phosphoric acid in a formation electrolyte in accordance with the present invention, it is preferred that not more than about three moles, more preferably about two moles, of amine base be used per mole of phosphoric acid in the formation electrolyte. Through the use of one of the afore-described amine additives to a phosphoric acid containing, substantially non-aqeous, polar aprotic formation electrolyte in accordance with this specification, solution resistivities as low as 1,000 ohms can be achieved. The breakdown voltage for those same amine/phosphoric acid containing formation electrolytes is typically greater than 300 volts.

Ureas and substitute ureas can also be employed advantageously in the phosphoric acid containing formation electrolytes used in the process of this invention to effect reduced electrolyte resistivity. Preferred water and formation-electrolyte-soluble ureas include urea, and methyl substituted ureas. Urea and tetramethyl urea are most preferred. The amounts of urea or substituted urea which can be added with advantage to the formation electrolyte ranges from a trace of such compositions up to an amount approaching the solubility limit of the urea compound in the formation electrolyte.

In practice the process of the present invention is performed in essentially the same way as prior art electrochemical anodization processes. The metal to be subjected to the anodization processes is immersed in a substantially non-aqueous polar aprotic formation electrolyte as described herein and connected electrically to the positive pole of an electric current source capable of supplying either a constant current (by voltage regulation) or by applying a constant or programmed increasing voltage to the cell during the anodization process. With a constant current source, the voltage across the electrolytic cell is gradually increased to maintain a pre-set current density as a metal oxide layer is built up on the anode. The anodization procedure is continued until the voltage has been increased to a pre-determined level which can be as high as the breakdown voltage of the formation electrolyte.

While it is not believed that the current densities is a critical aspect of the present process, where the process is being applied to a more reactive metal such as titanium or a titanium based alloy, current density during anodization is preferably maintained at a level below about 2 milliamperes per square centimeter and most preferably, it is held below about 1 milliampere per square centimet r. It is preferred that the temperature of the formation electrolyte be monitored and maintained bel w about 50°C during the present anodization process. For the efficient production of anodic oxide up n titanium, f r-

mation electrolyte temperature should be held between about 0°C and about 30°C. Agitation or rapid circulation of the formation electrolyte within the electrolytic cell helps to reduce thermal gradients within the cell and also promotes the uniformity of the anodic oxide film.

The present process can be used advantageously for the production of capacitor electrodes; valve metal sheets or foils anodized in accordance herewith are provided with an impervious, high quality, corrosion resistant dielectric oxide film. Anodized valve metal electrodes can be assembled using art-recognised capacitor construction techniques to provide capacitors characterised by long-life operability over a wide range of operating conditions (applied voltages, temperatures, etc.). Titanium and titanium alloy electrodes are effeciently anodized in accordance with this process, and they show particular advantage in unit capacitance and oxide quality over titanium electrodes anodized using aqueous formation electrolytes.

The present invention is further exemplified by the following detailed examples, which are not intended to limit the scope of the invention or claims thereof:-

Example 1

Two commercially pure (Tico) titanium strips 0.050" thick and approximately 15/16" wide were anodized, one each in the following two formation electrolytes:

Solution 1:	ethylene glycol	25 vol.%
	water (de-ionized)	74 vol.%
	phosphoric acid (conc)	1 vol.%
Solution 2:	N-methyl-2-pyrrolidone	plus

concentrated phosphoric acid in an amount required to adjust solution resistivity to 25,000 ohms at 25°C.

Solution 1 was found to have a resistivity of approximately 150 ohms. It is typical of formation electrolytes which have been used to anodize tantalum. Anodization of the titanium strips was carried out at a current density of 1 milliampere per square centimeter, and the solutions were maintained at 25°C with rapid circulation. Voltage breakdown of Solution 1 occurred at 37 volts after ten hours. No voltage breakdown of Solution 2 was noted at 600 volts. This illustrates the inferiority of traditional anodizing solutions compared to those of the present invention.

Example 2

The aprotic properties of propylene carbonate were evaluated by the addition of ammonium carbonate to a 3% solution of phosphoric acid in propylene carbonate. The propylene carbonate solution of concentrated phosphoric acid was found to react, but very slowly, with ammonium carbonate.

Two commercially pure (Tico) titanium strips 0.050" thick and approximately 15/16" wide were anodized, one each in the following two formation electrolytes;

Solution #1:	Propylene carbonate	98 vol %
	Phosphoric acid (conc)	2 vol %
Solution #2:	Dimethylsulfoxide	90 vol %
	Phosphoric acid (conc)	10 vol %

Solutions 1 and 2 had solution resistivities of 30,000 ohms and 20,000 ohms at 25°C, respectively. The titanium strips were anodized in the respective solution at a current density of 1 milliamp per square centimeter at 25°C with rapid solution circulation. The voltage breakdown of Solution 1 was 330 volts. Voltage breakdown of Solution 2 was greater than 600 volts.

Example 3

The superiority of phosphoric acid as the ionogen in formation electrolyte solutions for the anodization of titanium is demonstrated by the following experiment. A titanium strip was anodized in a solution of boric acid and dimethylsulfoxide at a constant current of 1 milliamp per square centimeter. No rise in voltage occurred. It can be concluded that any oxide formed in that formation electrolyte is either very conductive or it dissolves upon forming. This experiment was repeated with formation electrolyte solutions containing, as ionogens, substantial amounts of organic acids, including citric, oxalic, tartaric, and salicylic acid in conjunction with the solvents, temperatures, solution resistivities and current densities used in the present process. Under such conditions a highly unstable oxide results which detaches from the base metal upon standing for a period ranging from several minutes to several hours.

Example 4

To determine the relative capacitance of the anodic oxide films formed upon titanium and tantalum, one inch strips of commercially pure Tico titanium and Fansteel tantalum sheets were cleaned with tolu ne and acetone t rem ve organic surfac contamination. The strips were then an dized t 100 volts

at a current density of 1 milliampere per square centimeter. Total time of anodization was one hour in the following solutions with the results indicated:

Titanium

4-butyrolactone	90 vol. %
phosphoric acid	10 vol. %
Solution Resistivity: 10,000 ohms at	25°C
Anodization temperature:	25°C

Final current density:80 microamps per square centimeter

Tantalum

water (de-ionized)	99 vol. %
phosphoric acid	1 vol. %
solution resistivity: 61 ohms at	85°C
anodization temperature:	25°C

final current density: 23 microamps per square centimeter

The anodized strips were then each rinsed with de-ionized water and dried at room temperature. The capacitance of each was then measured with an H.P. 4261 A bridge at 120 Hz. (2 wire) employing a porous graphite hollow cathode and 10% phosphoric acid electrolyte.

Capacity of anodized titanium (6 volt bias): 1 microfarad per square centimeter.

Capacity of anodized tantalum (2.2 volt bias): 0.12 microfarad per square centimeter.

The foregoing results show an eight-fold advantage for titanium oxide film capacitance at this anodizing voltage.

Example 5

Commercially pure titanium (Tico) was cleaned for one hour in a solution consisting of equal volumes of nitric acid (70%) and hydrogen peroxide (30%). Strips of this material were then anodized in a prior art formation electrolyte solution (a variation of the electrolyte of Wainer - U.S. Patent No. 2,874,102) and in an electrolyte of the present invention:

Prior art electrolyte

ethylene glycol	50.0 vol. %
de-ionized water	49.9 vol. %
phosphoric acid	.1 vol %

Resistivity: 5800 ohms at 23°C

Electrolyte of the present invention

N-methyl-2-pyrrolidone	500 ml.
phosphoric acid (85%)	10 ml.
pyridine	10 ml.
de-ionized water	2 ml.

Resistivity: 16,000 ohms at 25°C

The anodization was conducted at constant current with unstirred solutions at 25°C.

Prior art

Current Density	1 mamp/cm
Rate of Δ Voltage	5 volts/min
Voltage at Δ Voltage ± 2 volts/min	465 volts

Time required to return to voltage (after 24 h urs of pen circuit) at 1 mamp/cm²: 285 seconds to 465 volts.

Present invention

Current Density	.5 mamp/cm²
Rate of Δ Voltage	6 volts/min
Voltage at × Voltage ± 2 volts/min	571 volts

Time required to return to voltage (after 24 hours of open circuit) at 1 mamp/cm² 135 seconds to 571 volts.

The efficiency of anodization with the prior art solution is only about 40% of that of the present solution. The evolution of gas at the anode accounts for the additional 60% of the current flow.

Example 6

The electrolyte of the present invention may be produced with a resistivity similar to those currently used to anodize tantalum and aluminium:

dimethylformamide	450.0 ml.
phosphoric acid	25.0 ml.
pyridine	12.5 ml.

Resistivity: 1,000 ohms at 30°C

A piece of titanium sheet, prepared as in Example 1, was anodized in the above solution at 25°C at a current density of .5 milliamperes per square centimeter. The breakdown voltage (unstirred solution) was 324 volts. Upon reapplication of voltage the breakdown voltage increased to 335 volts. The breakdown voltages listed above are the voltages at which the voltage drops (due to the constant current power supply) while gassing is observed at the anode accompanied by scintillation (sparking) which is observable in a dark room.

Example 7

A sheet of tantalum was anodized to 200 volts in .1% phosphoric acid at 85°C. For 25 square centimeters of the anodized surface capacitance = 1.62 microfarads or approximately 13 cv/cm² (microfarad volts per cm²).

A sheet of Tico titanium was anodized to 500 volts at .5 milliampere per square centimeter in the following solution:

N-methyl-2-pyrrolidone	500ml
pyridine	20 ml
phosphoric acid (85%)	10 ml
de-ionized water	2 ml

Resistivity: 11,500 ohms at 27°C

For 25 square centimeters of the anodized surface, capacitance = 20.1 microfarads or approximately 400 cv/cm². This indicates a cv/area advantage of approximately 30-fold for titanium vs. tantalum at 500 volts. The above measurements were made with an H.P. 4261 A bridge with a porous graphite cathode (2 wire connection) and 10% phosphoric acid electrolyte, 2.2 volt bias and 120 Hz.

Example 8

Zirconium foil (from Teledyne Wah Change Albany) was cleaned in nitric acid/hydrogen peroxide and then anodized in the following solution:

N-methyl-2-pyrrolidone	450.0 ml.
phosphoric acid (85%)	25.0 ml.
pyridine	12.5 ml.

Resistivity: 3,500 ohms at 25°C
Current Density: .5 milliamp per square centimeter
Anodization Voltage: 300 volts

After two hours at voltage, current = 10 microamps per square centimeter. The capacitance of the anodized zirconium strip measure at 1000 Hz., 2.2 volt bias = .06 microfarads/cm², 18 microfarad V/cm².

Example 9

A strip of commercially pure titanium, cleaned in nitric acid/hydrogen perioxide, was anodized in the following solution:

dimethylsulfoxide	500 ml.
phosphoric acid (85%)	24 ml
urea	50 gms
Resistivity: 8000 ohms at 25°C	

Anodization was conducted at 25-27°C and with a current of .5 milliamps per square centimeter to 500 volts. Direct current leakage in formation electrolyte:

70 microamps/cm^2 after 20 minutes at voltage

2 microamps/cm^2 after 9 hours at voltage

No corrosion or solid precipitation occurred. Although a lower ratio of urea to acid could easily be used, the present ratio was selected to illustrate the high solubility of urea in dimethylsulfoxide.

CLAIMS

1. A process for electrochemically forming a dielectric oxide film on a valve metal comprising subjecting said valve metal to electrolytic anodic oxide formation conditions in a substantially non-aqueous formation electrolyte, said electrolyte having a resistivity between 1,000 ohms and 30,000 ohms per cubic centimeter at 25°C, said electrolyte comprising a polar aprotic solvent and an ionogen comprising phosphoric acid or an electrolyte-soluble phosphate salt.

2. A process according to claim 1 wherein the formation electrolyte contains phosphoric acid and, in addition, urea, a water soluble substituted urea, or up to three moles of an amine base per mole of phosphoric acid in the formation electrolyte.

3. A process according to claim 2 wherein the formation electrolyte contains urea, tetramethyl urea or pyridine.

4. A process according to any one of claims 1 to 3 wherein the valve metal is selected from aluminium, titanium, niobium, tantalum, zirconium and alloys based on said valve metals.

5. A process according to claim 4 wherein the polar aprotic solvent is selected from dimethylformamide, dimethysulfoxide, N-methyl-2-pyrrolidone, 4-butyrolatone, propylene carbonate and mixtures thereof.

6. A process according to claim 1 wherein the valve metal is titanium or a titanium based alloy and the temperature of the formation electrolyte is maintained below about 50°C.

7. A process according to claim 6 wherein the formation electrolyte includes phosphoric acid in an amount sufficient to reduce the resistivity of the formation electrolyte to between 10,000 and 30,000 ohms.

8. A process according to claim 7 wherein the polar aprotic solvent is dimethylformamide, dimethylsulfoxide, N-methyl-2-pyrrolidone, 4-butyrolactone, propylene carbonate or a mixture of any of these.

9. A process according to claim 7 wherein during electrolyte anodic oxide formation, a current density of not greater than 2 milliamperes per square centimeter is maintained by increasing anodic formation voltage to a level not exceeding the breakdown voltage of the formation electrolyte.

10. A process according to claim 9 wherein the temperature of the formation electrolyte is maintained between 0°C and 30°C, and the current density is not greater than 1 milliampere per square centimeter.

11. A process according to claim 2 wherein the valve metal is titanium or a titanium based alloy and the temperature of the formation electrolyte is maintained below 50°C.

12. A process according to claim 11 wherein the formation electrolyte (1) contains urea, tetramethyl urea, or pyridine; (2) has a breakdown voltage greater than 200 volts; and (3) has a resistivity between 1,000 ohms and 30,000 ohms.

13. A process according to claim 12 wherein during anodic oxide formation, a current density of not greater than 2 milliamperes per square centimeter is maintained by increasing anodic formation voltage to a level not exceeding the breakdown voltage of the formation electrolyte.

14. A process according to claim 13 wherein the temperature of the formation electrolyte is maintained between 0°C and 30°C.

15. A process for anodizing titanium metal or titanium metal based alloys wherein the metal is subjected to electrolytic anodic oxide formation conditions in a formation electrolyte, at a current density of not greater than 2 milliamperes/cm^2 in a substantially non-aqueous polar aprotic formation electrolyte containing an ionogen comprising phosphoric acid or an electrolyte-soluble phosphate salt.

16. A process according to claim 15 wherein the formati n electrolyte has a resistivity between 1,000 ohms and 30,000 ohms.

17. A process according to claim 15 wherein the formation electrolyte contains a ph sph ric acid and, in addition, urea, a water soluble substituted urea, or up t three moles f an amine base per m le f phosphoric acid in the formation electrolyte, said amine bas being selected fr m electrochemically stable amine bases which form phosphate salts soluble in both the formation electrolyte and water.

18. A process according to claim 15 wherein the formation electrolyte contains ph sphoric acid and,

in addition, urea, or up to three moles of pyridine per mole of phosphoric acid in the formation electrolyte.

19. A process according to claim 20 wherein the formation electrolyte contains about two moles of pyridine per mole of phosphoric acid in the formation electrolyte.

20. A process for electrochemically for a dielectric oxide film on a valve metal substantially as hereinbefore described in any one of Examples 1 (solution 2), 2, 4 (Titanium), 5 (present invention), 6, 7 (Titanium), 8 and 9.

21. A valve metal electrode for a capacitor anodized by a process according to any one of claims 1 to 20.

22. An electrolytic capacitor comprising a valve metal electrode according to claim 21.

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